Refractory Complex Concentrated Alloys (RCCAs)

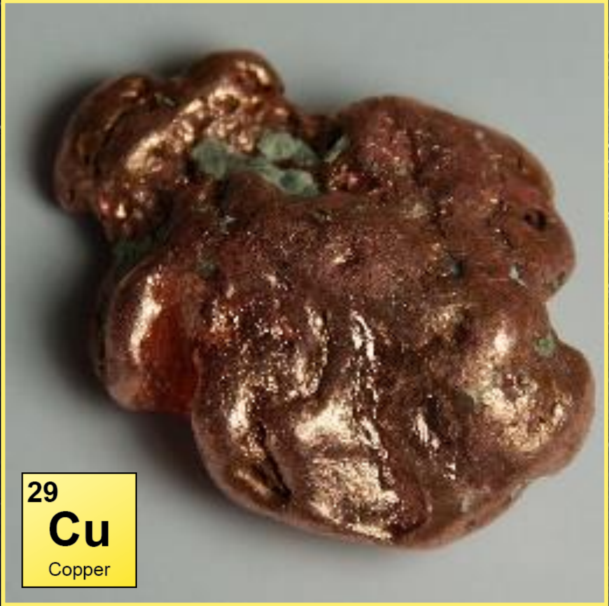
ARPA-E Workshop
20,21 November 2019

Dr. D.B. Miracle and Dr. O.N. Senkov

Air Force Research Laboratory
Materials and Manufacturing Directorate, Dayton, OH USA

The history of metallic alloys

Stone Age



Bronze Age

Iron Age

13 **Al** Aluminum

27 **Co** Cobalt

12 **Mg** Magnesium

42 **Mo** Molybdenum

41 **Nb** Niobium

28 **Ni** Nickel

22 **Ti** Titanium

29 **Cu** Copper

82 **Pb** Lead

79 **Au** Gold

47 **Ag** Silver

50 **Sn** Tin

80 **Hg** Mercury

26 **Fe** Iron

30 **Zn** Zinc

-9000 -8000 -7000 -6000 -5000 -4000 -3000 -2000 -1000 0 1000 2000

Two Big Ideas

"…to investigate the unexplored central region of multicomponent alloy phase space."

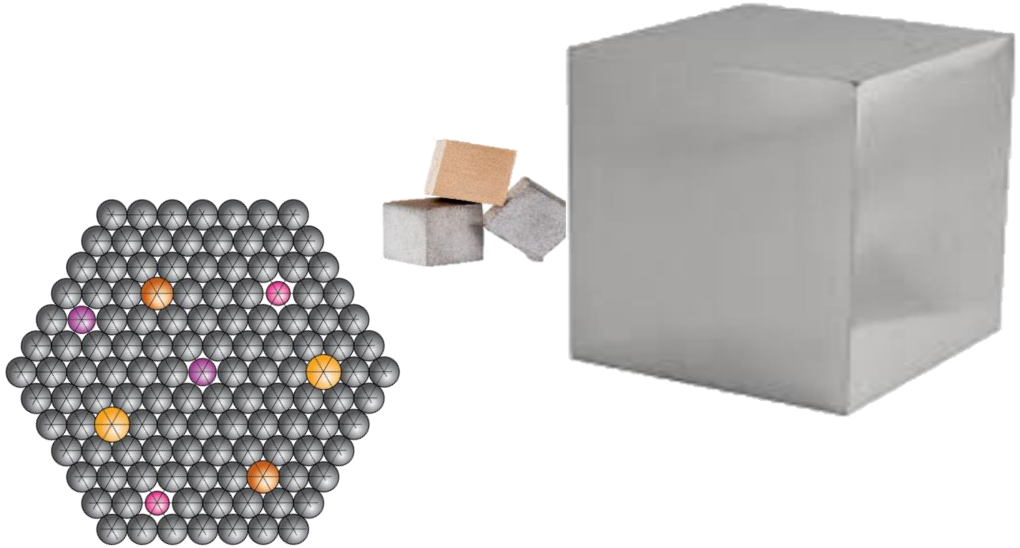
Cantor *et al.*, *Mat. Sci. Eng. A*, **375-377**, 213 (2004).

- Vast opportunity to discover new alloys of scientific and practical benefit

Favor solid solution over intermetallic phases thru configurational entropy

- Vary entropy thru the number and concentrations of principal elements ($N \geq 5$)

Yeh *et al.*, *Adv. Eng. Mat.*, **6**, 299 (2004). Plus many others…



Both ideas focus on concentrated, multi-component alloys bases

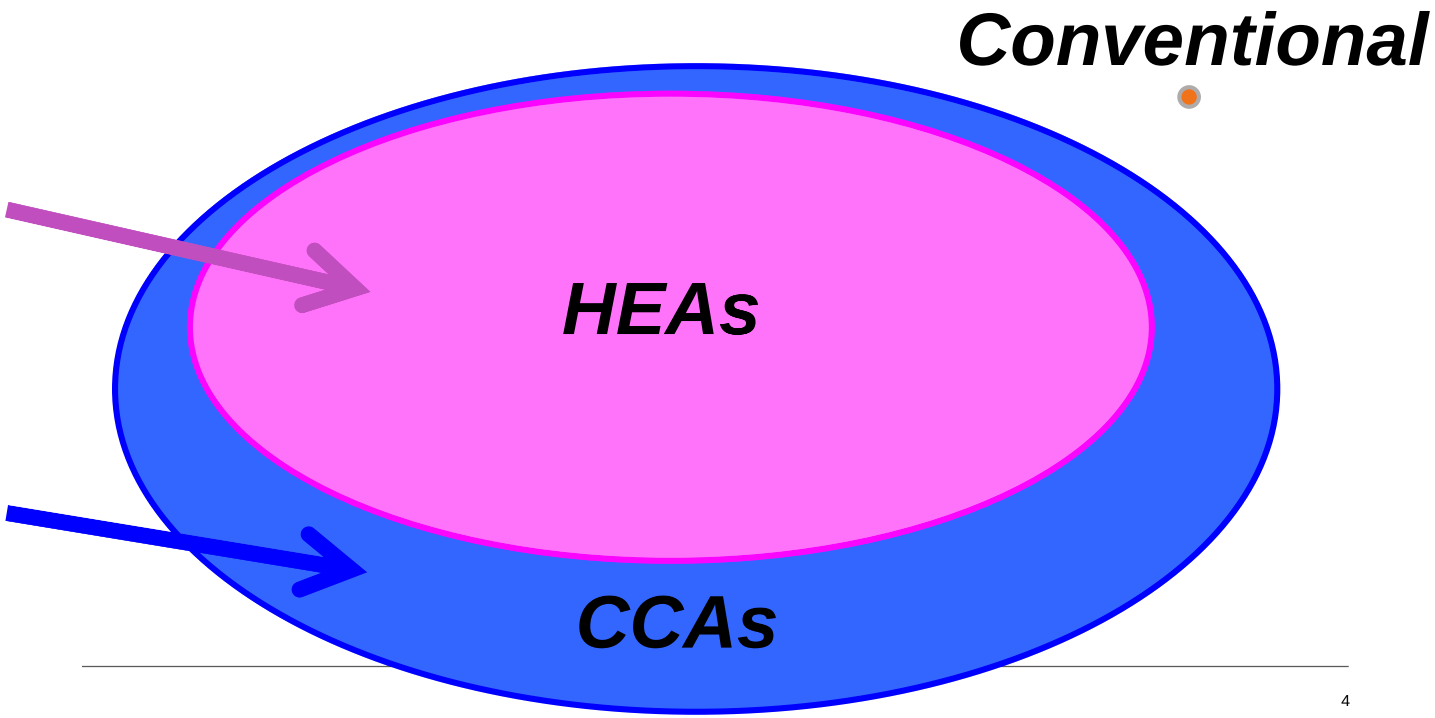
HEAs and Complex, Concentrated Alloys (CCAs)

Attractive properties are found in alloys with *N* < 5, with concentrations >35% and in microstructures with more than a single solid solution phase

Terms such as CCAs and multi-principal element alloys (MPEAs) further expand the possibilities

- *5 or more elements*
- *Nominally single-phase*
- *High configurational entropy*

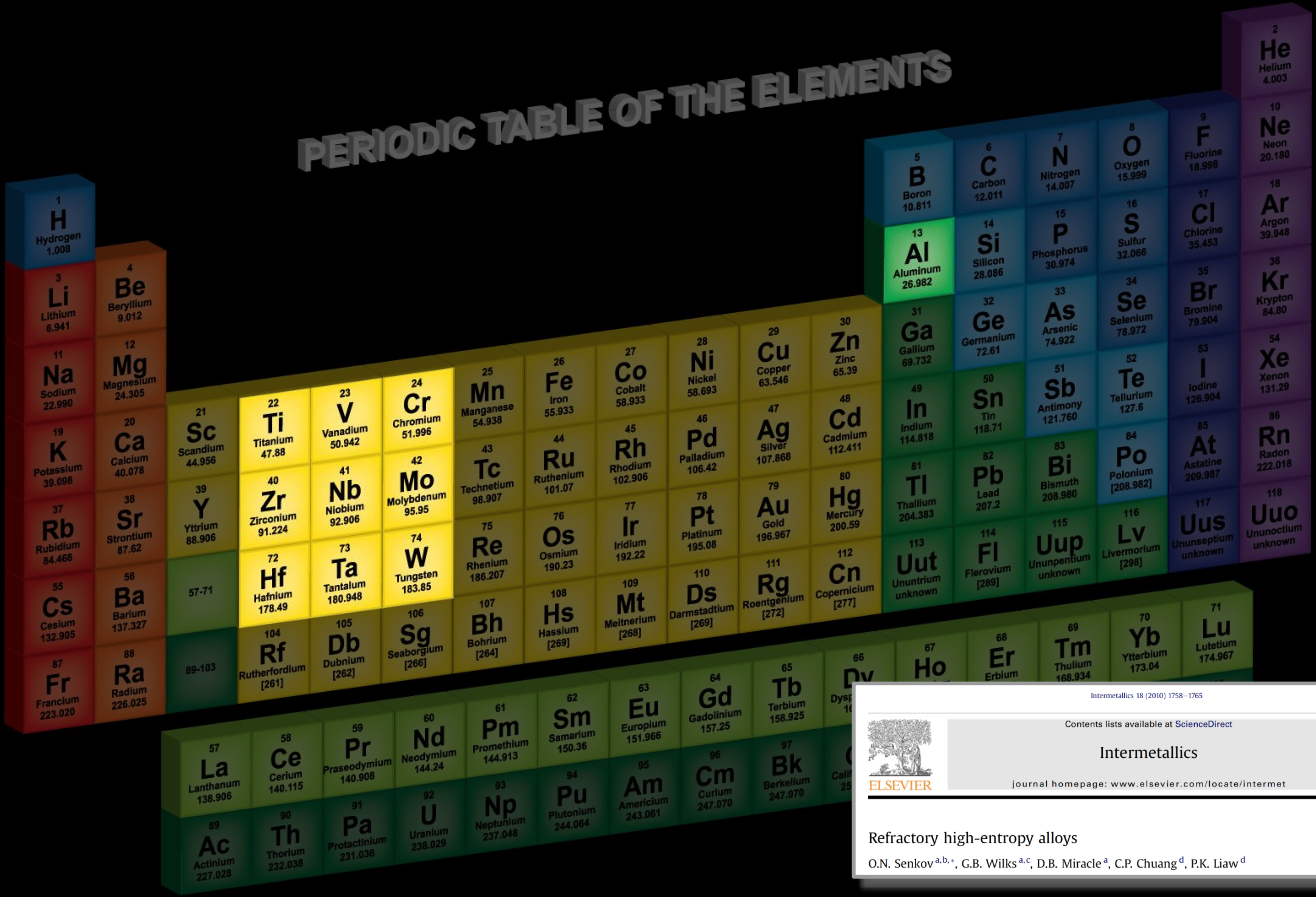
- *May have <5 elements*
- *Can have >35% of elements*
- *Can have multiple phases*
- *Entropy doesn't matter*



High temperature metals remain a high impact, long-sought, unsatisfied challenge

“. . . but metal is in the heart of that machine. In all your machines, wherever you use fire and heat to make things move, there is metal.”

Orson Scott Card, from “Speaker for the Dead” (1986)



Intermetallics 18 (2010) 1758–1765

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Refractory high-entropy alloys

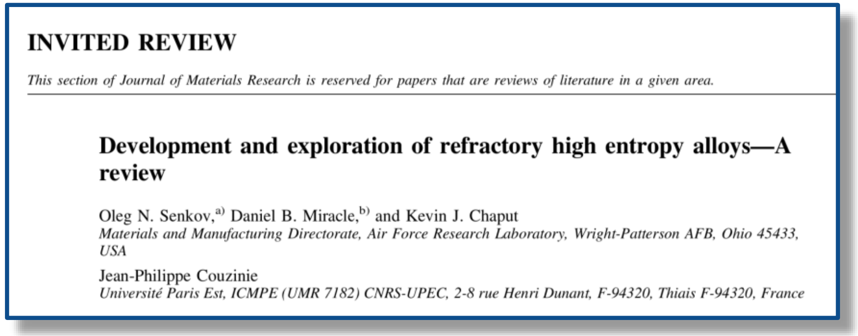
O.N. Senkov [a,b,*], G.B. Wilks [a,c], D.B. Miracle [a], C.P. Chuang [d], P.K. Liaw [d]

Common RCCAs and principal element combinations

Common 3 principal elements are (Nb,Ti,Zr), (Mo,Nb,Ti), (Nb,Ti,V)

Common 4 principal elements are (Mo,Nb,Ti,Zr), (Mo,Nb,Ti,V), (Nb,Ti,V,Zr)

The most common RCCAs are HfNbTaTiZr, MoNbTaW, MoNbTaVW, NbTiVZr and $AlMo_{0.5}NbTa_{0.5}TiZr$

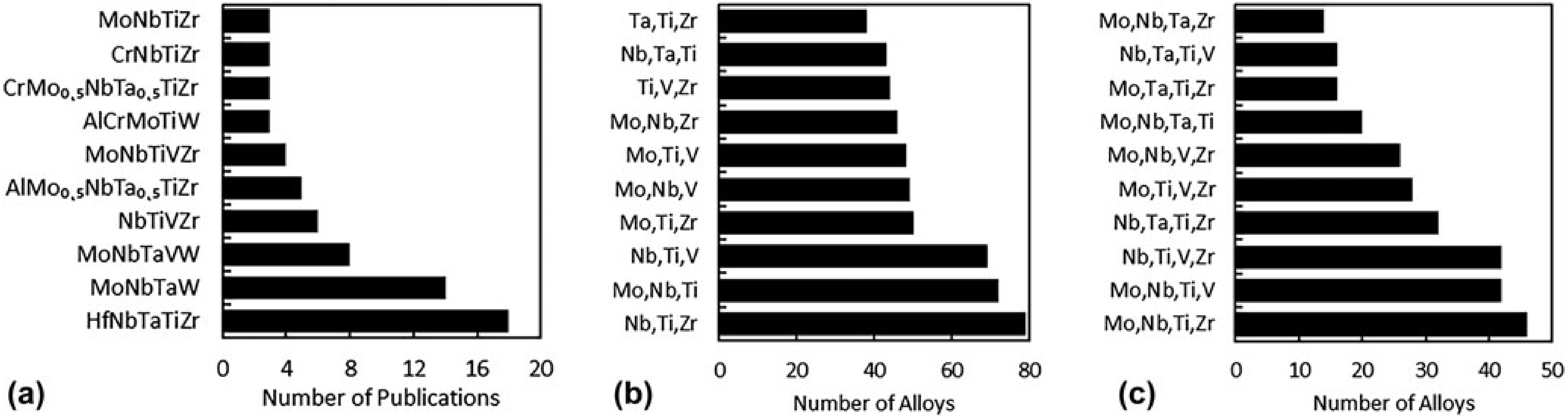

INVITED REVIEW

This section of Journal of Materials Research is reserved for papers that are reviews of literature in a given area.

Development and exploration of refractory high entropy alloys—A review

Oleg N. Senkov,[a] Daniel B. Miracle,[b] and Kevin J. Chaput
Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, Ohio 45433, USA

Jean-Philippe Couzinie
Université Paris Est, ICMPE (UMR 7182) CNRS-UPEC, 2-8 rue Henri Dunant, F-94320, Thiais F-94320, France



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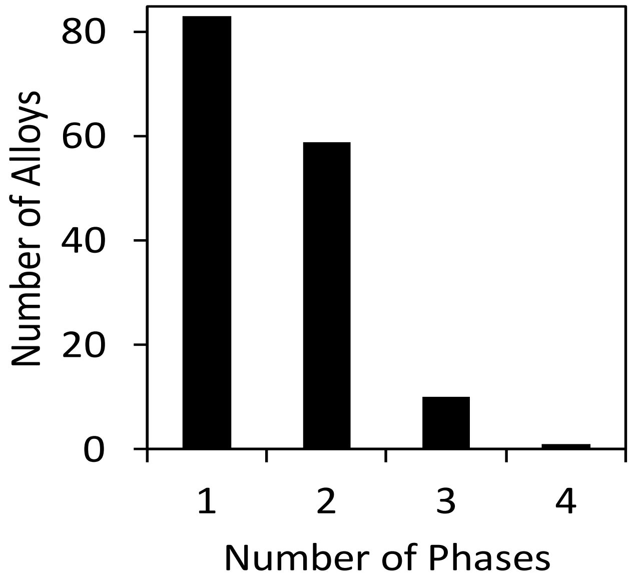
Number and types of RCCA phases



1-phase BCC microstructures comprise 54% of RCCAs

- Most (57) contain only elements from subgroups IV-VI, but 24 contain Al, which stabilizes BCC structure in Hf, Ti and Zr

2-phase microstructures give 39% of RCCAs

- The matrix phase is BCC (48 alloys), B2 (8 alloys) or FCC (3 alloys)

3- and 4-phase alloys give 7% of RCCAs

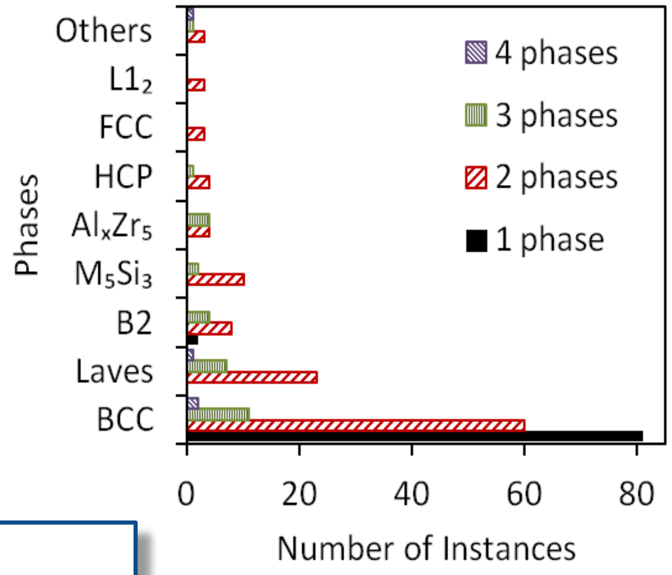
Disordered BCC is the most common phase

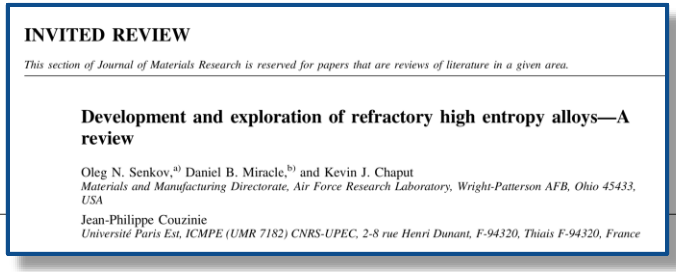
Laves (C14 or C15) is the 2nd most common

- Laves is always associated with Cr, Mo and Zr, and/or a combination of Al, V and Zr

B2 often gives an RCCA 'superalloy' microstructure

- The main elements are Al, Nb, Ta and Zr

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HEA Property Comparison

RHEAs offer potential for improved high temperature strength and specific strength relative to superalloys and conventional refractory alloys


INVITED REVIEW

This

Acta Materialia 135 (2017) 177–187

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

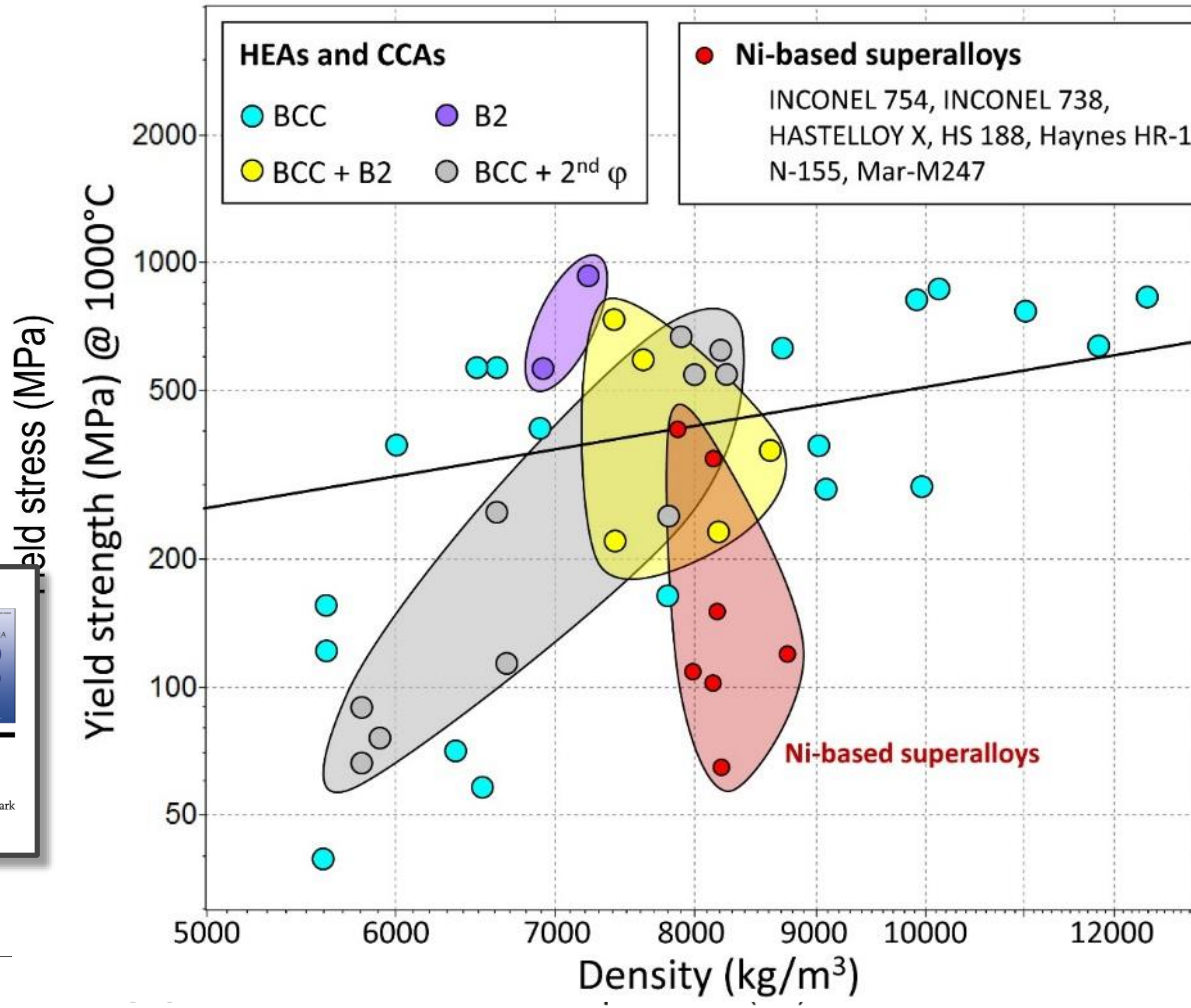
ELSEVIER

Full length article

Mapping the world of complex concentrated alloys

Stéphane Gorsse [a, b, c, *], Daniel B. Miracle [d], Oleg N. Senkov [d]

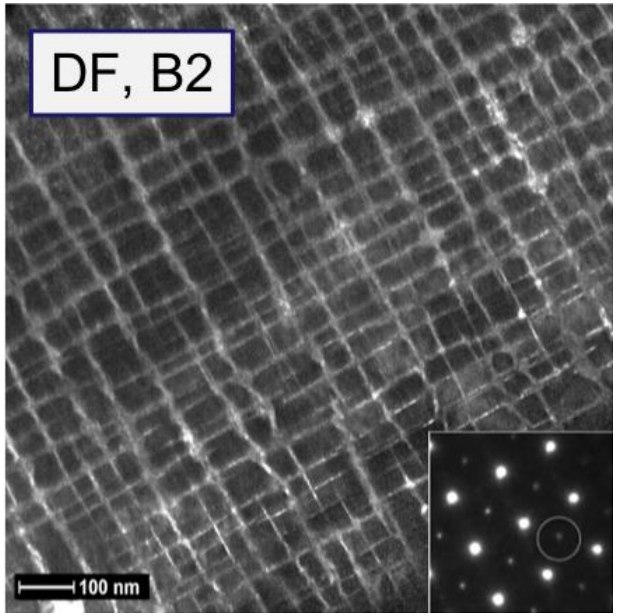
Diao, Feng, Dahmen, Liaw, COSSMS, 21 (2017) 252



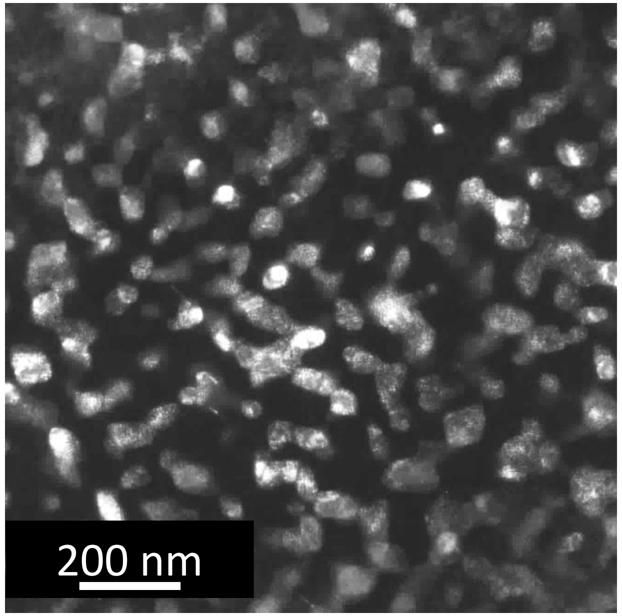
Refractory CCA Superalloys (RSAs)

Two-phase BCC+B2 alloys with atomically coherent, nanometer sized particles are similar to γ/γ' superalloy microstructures

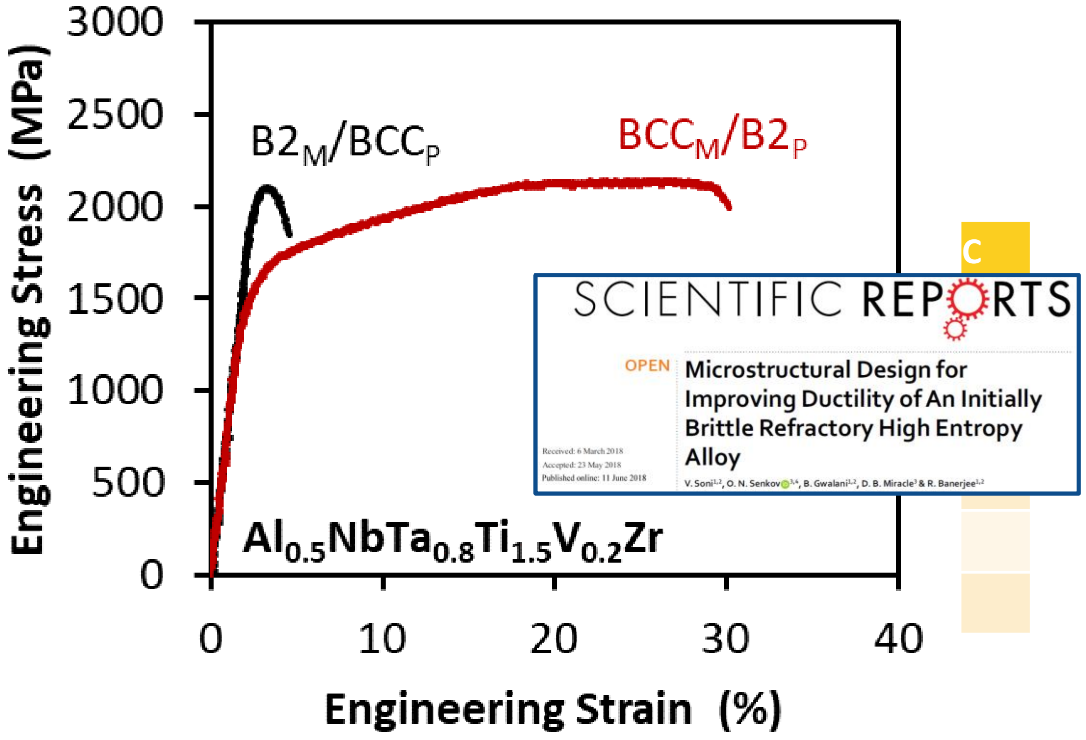
- B2 is typically the continuous phase but the microstructure can be inverted
- RSAs are among the highest strength RCCAs and also have improved oxidation resistance
- RSAs include $AlMo_{0.5}NbTa_{0.5}TiZr$; $Al_{0.3}NbTaTi_{1.4}Zr_{1.3}$; $Al_{0.5}NbTa_{0.8}Ti_{1.5}V_{0.2}Zr$; $Al_{0.5}Mo_{0.5}NbTa_{0.5}TiZr$



B2 matrix + BCC cuboidal precipitates (brittle)



BCC matrix + B2 spherical precipitates (ductile)



High Entropy Ceramics

Ordered compounds with ionic/covalent bonding

MPEAs are an alloying approach, not a family of alloys, so CCAs include other inorganic materials

The MPEA field includes ceramic materials such as oxides/ borides/ nitrides/ carbides

nature COMMUNICATIONS

ARTICLE

Received 8 Apr 2015 | Accepted 25 Aug 2015 | Published 29 Sep 2015

DOI: 10.1038/ncomms9485

OPEN

Entropy-stabilized oxides

Christina M. Rost[1], Edward Sachet[1], Trent Borman[1], Ali Moballegh[1], Elizabeth C. Dickey[1], Dong Hou[1], Jacob L. Jones[1], Stefano Curtarolo[2] & Jon-Paul Maria[1]

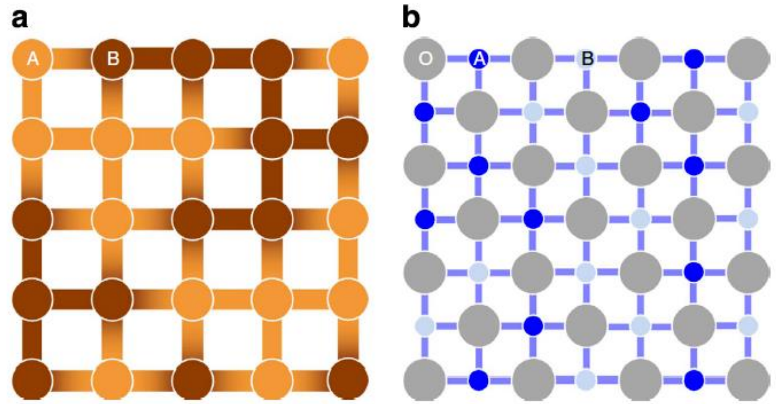


Figure 6 | Binary metallic compared with a ternary oxide. A schematic representation of two lattices illustrating how the first-near-neighbour environments between species having different electronegativity (the darker the more negative charge localized) for (**a**) a random binary metal alloy and (**b**) a random pseudo-binary mixed oxide. In the latter, near-neighbour cations are interrupted by intermediate common anions.

Environmental resistance

Four degradation mechanisms

Solid solution interstitial hardening and embrittlement

- Rapid bulk diffusion produces thick, brittle surface layers in some refractory metals/alloys (alpha case in titanium alloys)

Pest attack in some refractory metal aluminides, silicides

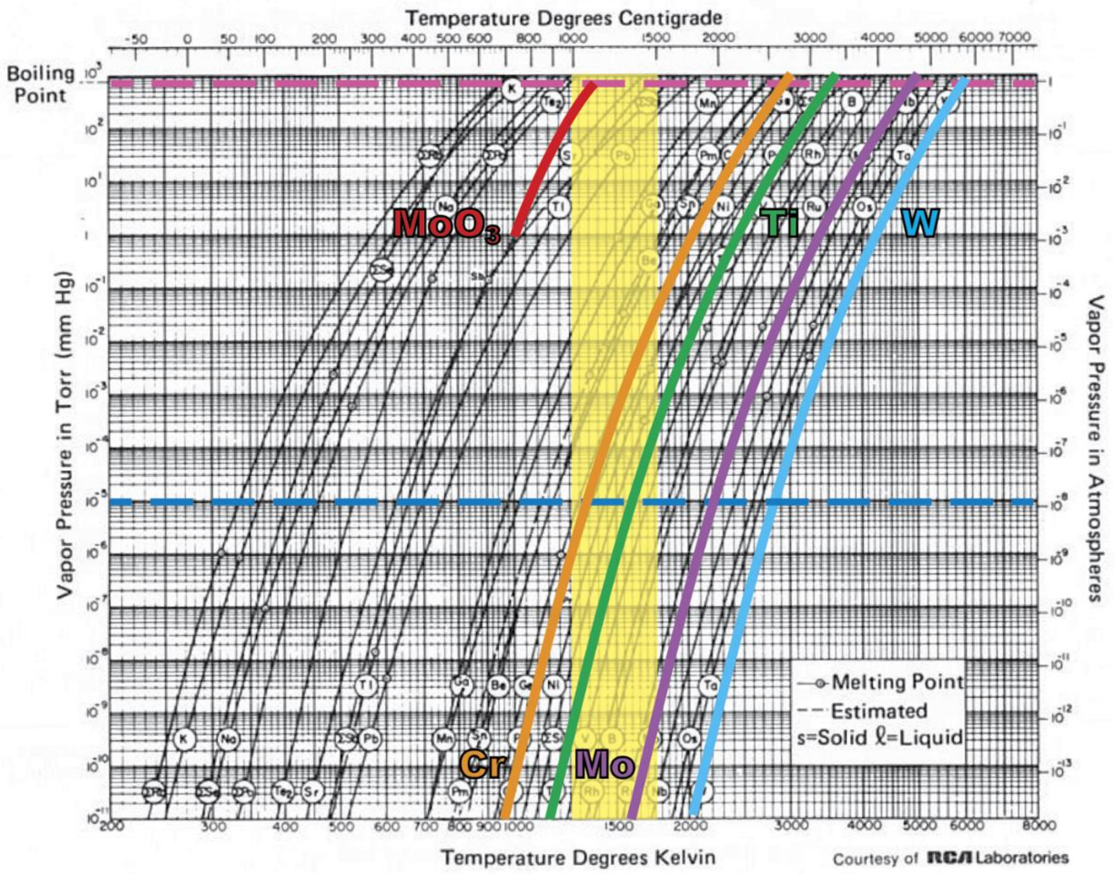
- Grain boundary oxidation near ~700°C produces internal stresses that eject grains

Volatilization

- Elemental Cr and MoO_3 have high vapor pressures

Rapid, non-protective oxide formation

- Includes internal oxidation



Complex, concentrated alloys (CCAs)

How are they different?


Journal of Alloys and Compounds 729 (2017) 1004–1019
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Journal of Alloys and Compounds
journal homepage: http://www.elsevier.com/locate/jalcom

High temperature oxidation behaviors of equimolar NbTiZrV and NbTiZrCr refractory complex concentrated alloys (RCCAs)

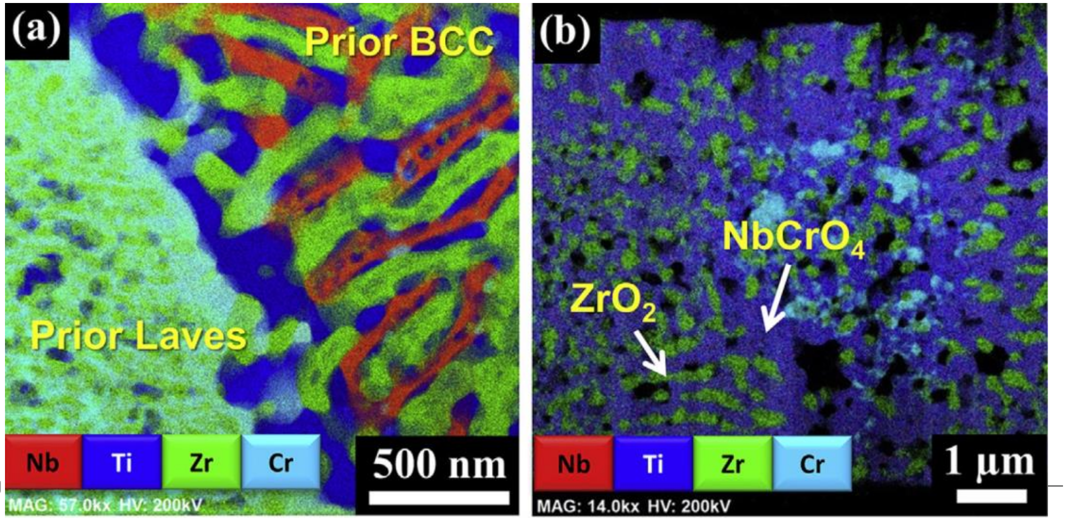
T.M. Butler [a,*], K.J. Chaput [a], J.R. Dietrich [a], O.N. Senkov [a,b]

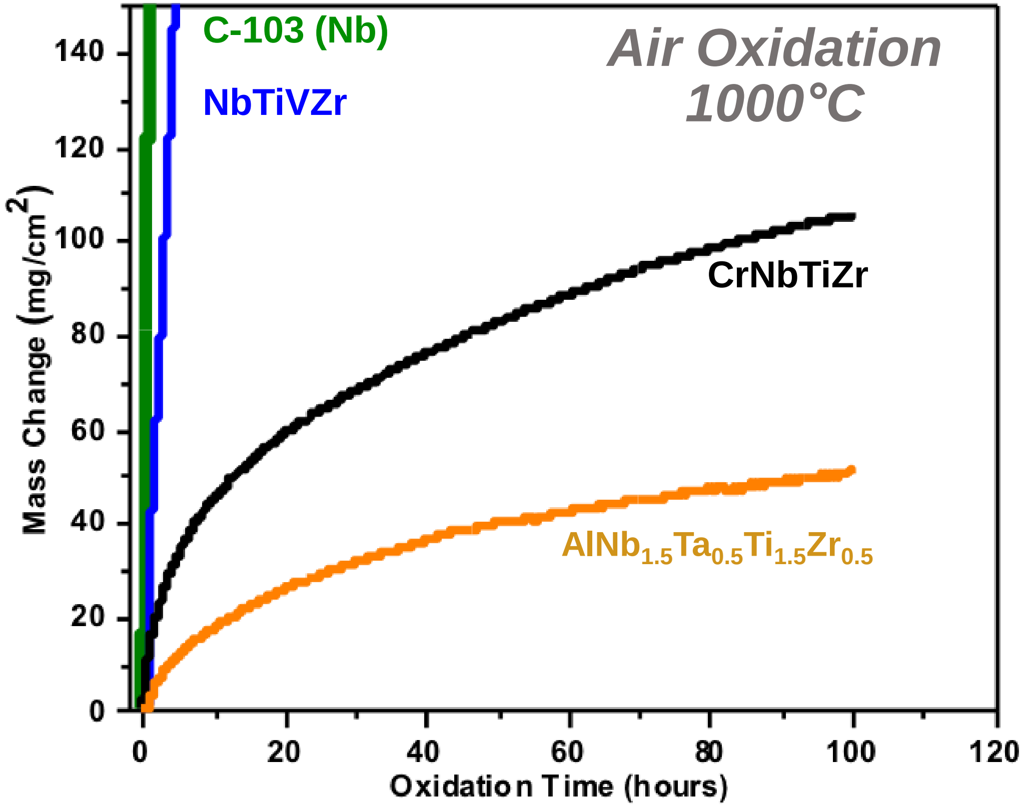
Exceptional oxidation resistance in refractory CCAs

- Parabolic kinetics that 100 times slower than conventional refractory alloys

CrNbTiZr

4 hr | 100 hr





Brittle to ductile transition (BDT)

Competition between yield and fracture

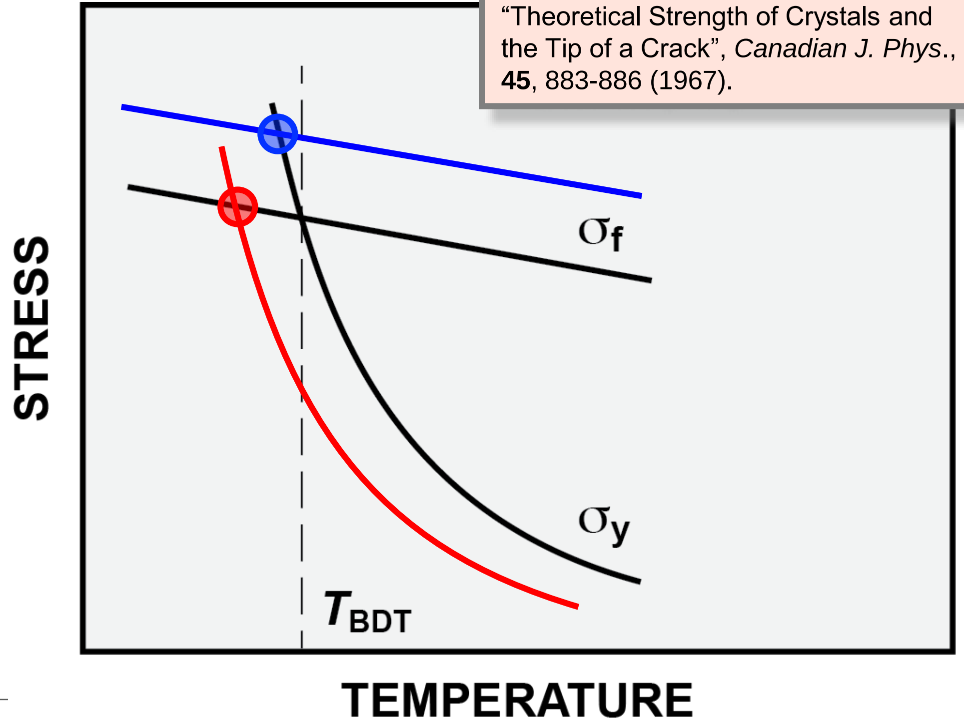
In BCC metals, fracture stress (σ_f) is relatively insensitive to *T* but yield stress (σ_y) depends strongly on *T*

- A brittle-to-ductile transition temperature (T_{BDT}) exists, below which fracture precedes bulk plastic deformation
- Increasing σ_f and decreasing σ_y decreases T_{BDT}

Other parameters also decrease T_{BDT}

- Increasing elastic modulus or surface energy
- Decreasing shear modulus or lattice constant
- Decreasing grain size

Designing RCCAs with these approaches may give T_{BDT} < RT



A. Kelly, W.R. Tyson and A.H. Cottrell; "Theoretical Strength of Crystals and the Tip of a Crack", *Canadian J. Phys.*, **45**, 883-886 (1967).

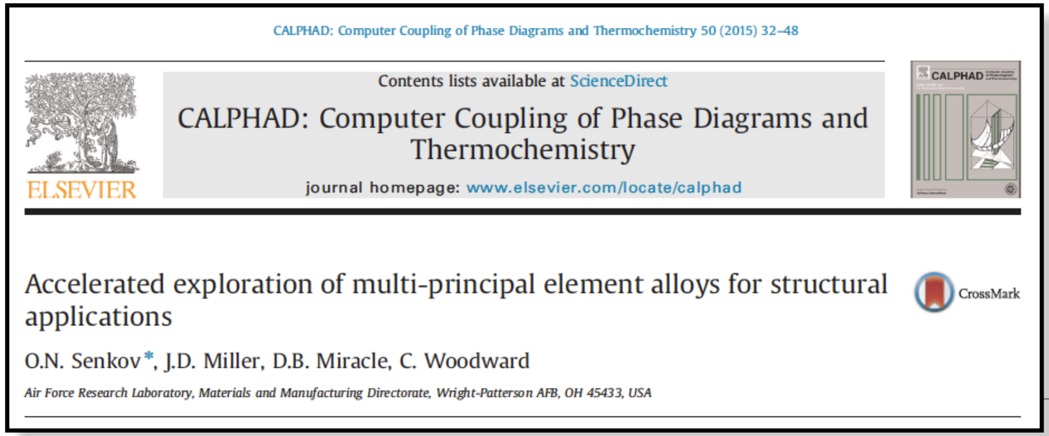
AFRL

Large number of alloy systems

CCAs offer a cosmically vast number of new alloy bases to explore

New strategies & tools can accelerate development by synergizing hi throughput computations & experiments

- CALPHAD calculations can significantly accelerate exploration but thermodynamic databases for refractory elements need improvement
- High throughput experiments are needed, especially for environmental resistance and tensile ductility


CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 50 (2015) 32–48

Contents lists available at ScienceDirect

CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

journal homepage: www.elsevier.com/locate/calphad

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Accelerated exploration of multi-principal element alloys for structural applications

O.N. Senkov *, J.D. Miller, D.B. Miracle, C. Woodward

Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH 45433, USA


Scripta Materialia 127 (2017) 195–200

Contents lists available at ScienceDirect

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Viewpoint Article

New strategies and tests to accelerate discovery and development of multi-principal element structural alloys

Daniel Miracle [a,*], Bhaskar Majumdar [b], Katelun Wertz [a], Stéphane Gorsse [c,d,e]

Simplification by palette selection

Refractory CCAs (RCCAs)


J. Mater. Res., Vol. 33, No. 19, Oct 14, 2018

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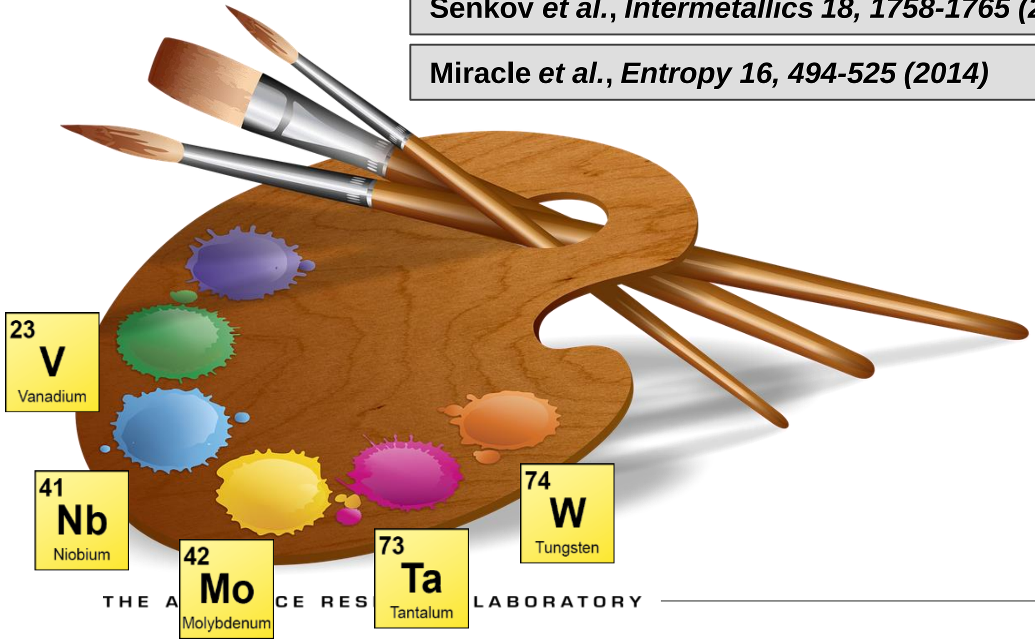
Refractory metals, conventional high temperature alloy elements (Co, Ni) and compound-forming elements (Al, Si, C, N…)

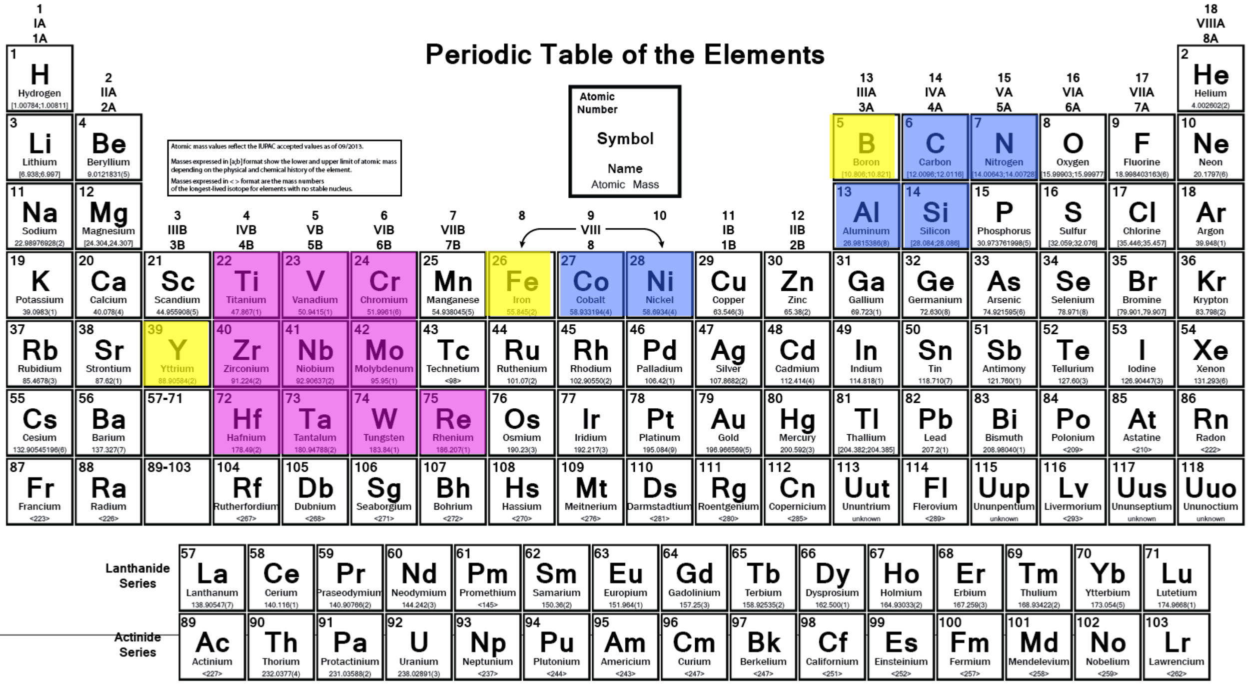
May also consider elements with high T_m and low cost, density (B, Fe, Y…)

This palette gives 'only' 43,605 bases with 3-6 principal elements

Senkov *et al.*, *Intermetallics 18, 1758-1765 (2010)*

Miracle *et al.*, *Entropy 16, 494-525 (2014)*





New strategies are being proposed

Simplify by separating composition, microstructure evaluations

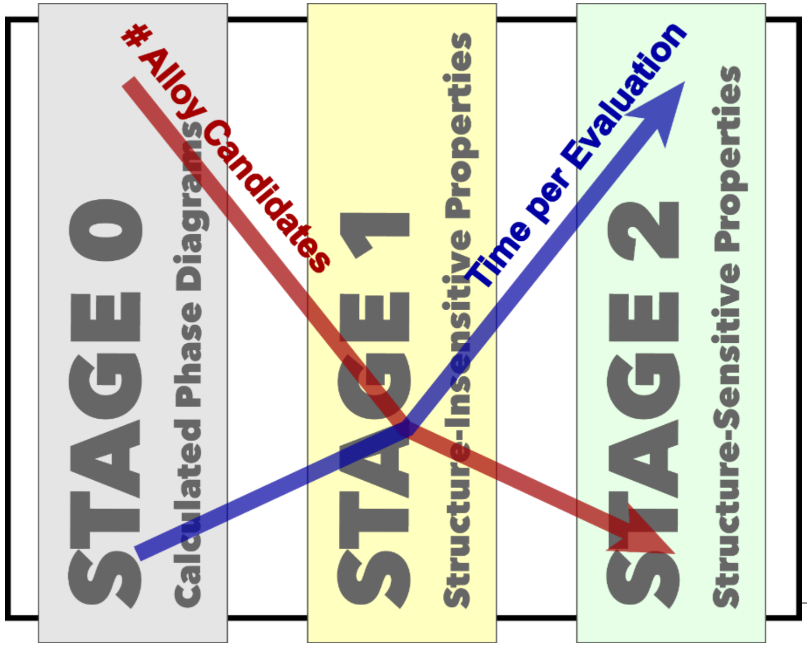
Evaluations that reject the largest number of alloys with the smallest effort are done first

New Characterization Strategy

Stage 0
- Hi throughput computations

Stage 1
- Microstructure-insensitive properties
- Environmental resistance, T_m
- Modulus, density, thermal properties

Stage 2
- Microstructure-sensitive properties
- Tensile strength and ductility…

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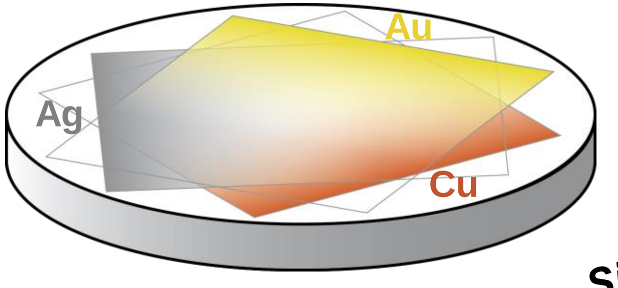
High throughput experiments

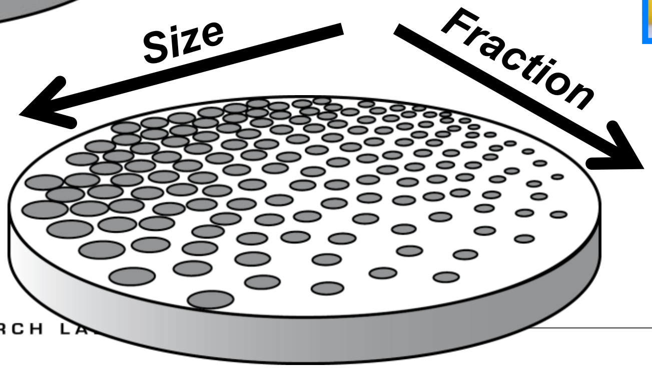
Don’t exist for structural materials due to microstructure, length scale issues

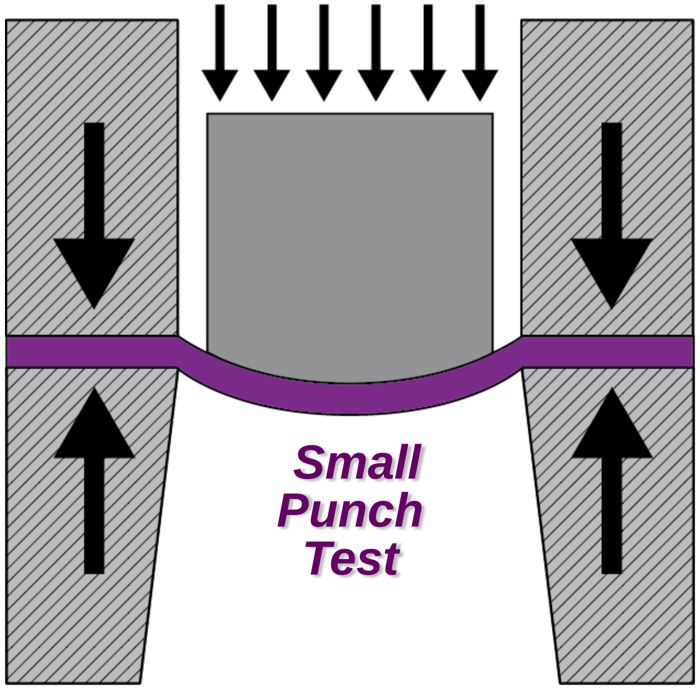
- Tensile properties and environmental resistance are top priorities

New approaches for materials libraries are needed

- Graded composition, graded microstructure and ‘materials on demand’ (candy dot)
- Bulk-like libraries (not thin films) for mechanical properties
- Emerging capabilities may make these feasible







Back to the Future – *Fundamental data*

Current scientific progress is built upon fundamental data and knowledge collected more than 50 years ago

- Thermodynamic data and phase equilibria
- Phase transformations and phase stability
- Defects and defect energies (point, line, planar)
- Diffusion data and kinetic models
- Deformation mechanisms under different loading conditions
- *… and the influence of composition on the properties above!*

These data typically describe alloys with a single dominant solvent

It has become difficult to fund research collecting fundamental data

The materials community must once again embrace the collection of fundamental data, especially in concentrated alloys

Back to the Future – *Materials screening*

Materials screening used to be an important tool in materials research, but now…

- Funding agencies view screening as applied work, or mere phenomenology
- Many researchers avoid screening due to lower accuracy than more time-consuming methods

Screening allows researchers to quickly focus their efforts on materials that are most likely to have a significant impact on society!

We need to re-invigorate screening as an essential tool in basic science

- Better targets R&D resources to develop the most impactful knowledge
- Current R&D methods have inherent risks that are usually ignored

Imagine a 1 hour test with 100 questions…

Is it better to spend all your time on 1 question and be 99% sure of the answer…

…or would you rather be 70% sure of your answers for all 100 questions?

Closing remarks

HEAs/ CCAs change a 5,000 yr paradigm for developing materials

HEAs/ CCAs offer new challenges from vastness and new physical phenomena

Refractory CCAs offer significant promise but also three major technical challenges:

- environmental resistance (four distinct mechanisms)
- brittle-to-ductile transition (common to all BCC alloys)
- large number of new alloy bases to explore

New high throughput strategies and tests are needed (*back to the future*)

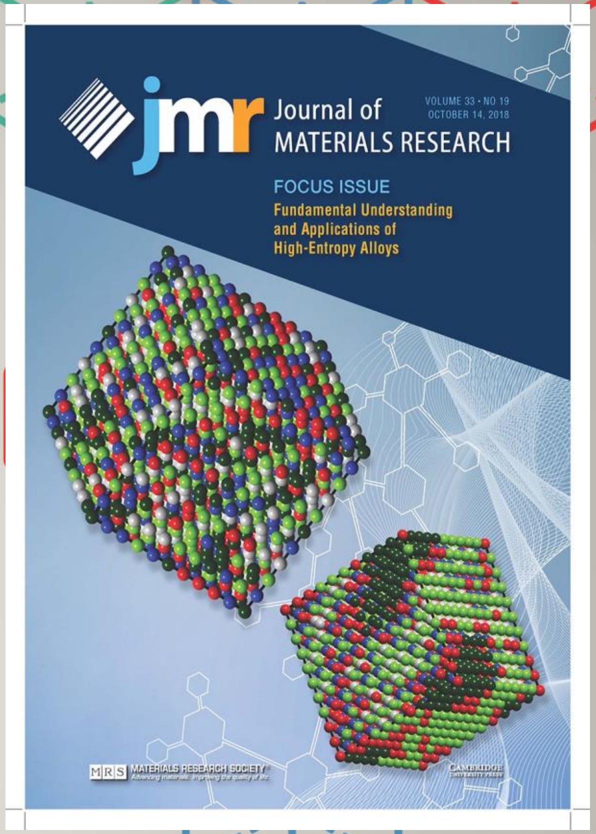
WORLD CONGRESS ON

HIGH ENTROPY ALLOYS HEA2019

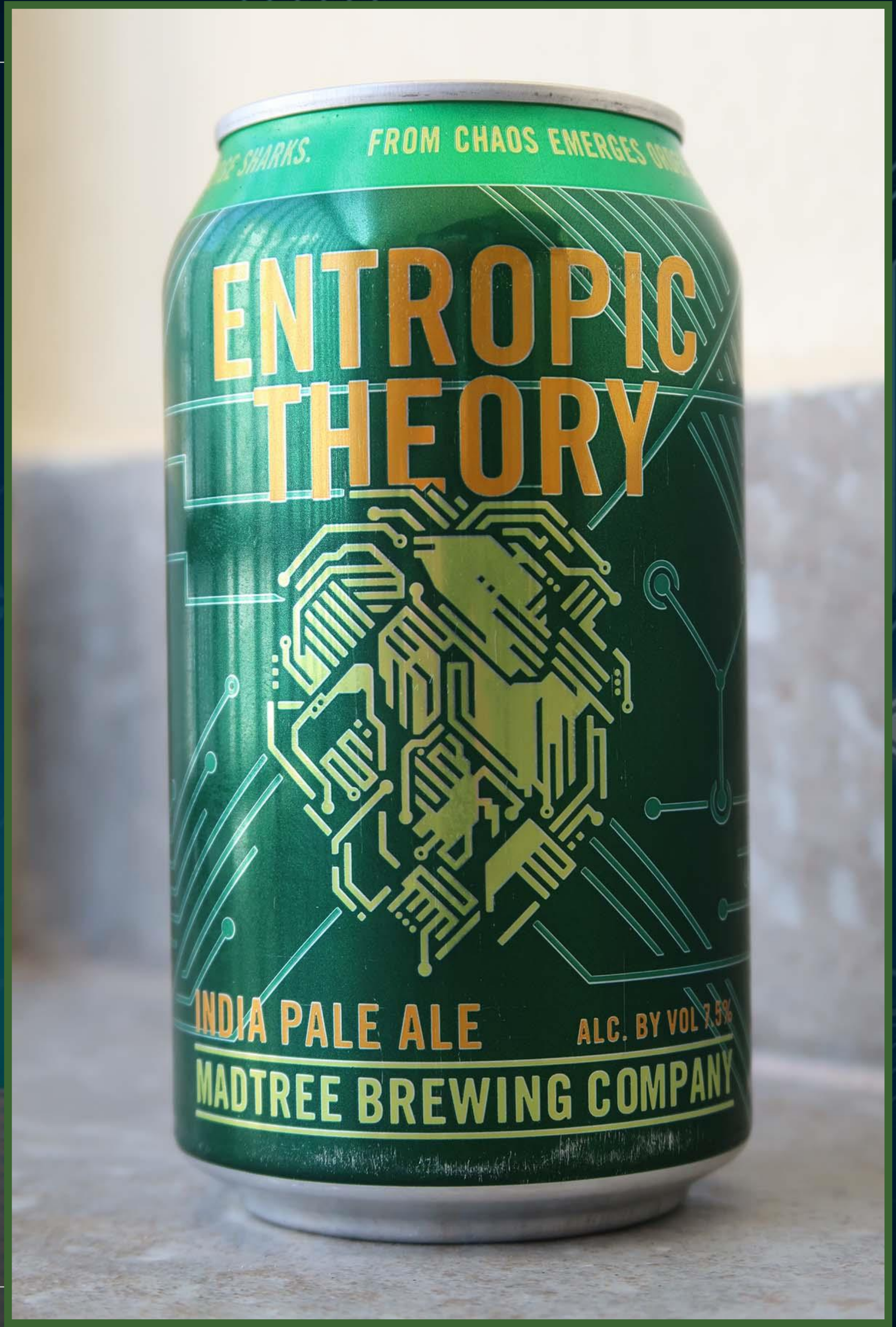
November 17–20, 2019

Seattle, Washington, USA

www.tms.org/HEA2019



Questions?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